

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) PHOTOTROPIC UNITS

(71) We, LIBBEY-OWENS-FORD COMPANY, formerly Libbey-Owens-Ford Glass Company a Corporation organized under the laws of the State of Ohio, United States of America, of 811 Madison Avenue, City of Toledo, County of Lucas, and State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates broadly to phototropic bodies and more particularly to a body of this character that is suitable for use as a lamina or interlayer in a laminated safety glass unit.

Laminated safety glass is probably best known for its use in the automotive field and for that purpose is generally made up of two sheets of glass with an interposed layer of plastic all bonded together under heat and pressure into a unitary structure.

However, in aircraft glazings for example, a considerable number of glass sheets may be combined with a corresponding number of plastic interlayers while, for other uses, single plastic sheets, laminations of plastic sheets only and simple glass to plastic laminations may be used.

This invention has for an object to provide first, a phototropic body e.g. a sheet that can be satisfactorily employed in connection with any of the above and, second an improved form of laminated safety glass unit having remarkably good and long-lasting phototropic properties.

The desirability of providing a laminated safety glass unit for a variety of applications in which the plastic interlayer is phototropic

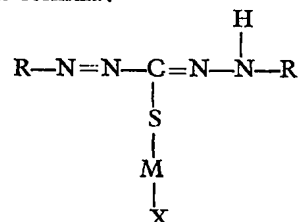
and/or thermotropic has been recognized as has also the phototropic properties of some metal dithizonates when incorporated into certain types of plastics.

However, prior to the present invention, no phototropic laminated safety glass commercially satisfactory for automotive glazing was available and the use of metal dithizonates were considered to be unsuitable as phototropic materials when contained in the plasticized resin plastics commonly and most widely used in making commercial laminated safety glass.

It is accordingly a further object of this invention to provide a phototropic plastic material which, in sheet form is useable either alone or as a commercially practicable component of a stable, tightly bonded glass-plastic lamination.

Another object is the provision of a phototropic glazing unit that embodies such a plastic sheet and possesses notably improved color, faster responses and longer effective life than heretofore available in units of this character.

According to the invention a phototropic unit comprises a body of plastics material combined with metal dithizonate rendering said body phototropic and having the following structural formula:



where M is an element selected from the

group consisting of bismuth, cadmium, cobalt, copper, gold, indium, iron, lead, manganese, mercury, nickel, palladium, platinum, polonium, silver, tellurium, thallium, tin and zinc; where R is an aryl group; and X is a radical containing a group selected from those consisting of carboxyl, ether, ester, amide, imide, nitrile, anhydride, amine, nitrate, acrylate, methacrylate, pyridyl sulfonate, isocyanate, thiocyanate, cyanide, molybdate, and tungstate.

These materials may be used to render the plasticized plastic phototropic in a number of different ways, for example by applying them in solution or in suspension to the surface of the sheeted plastic or to a second plastic or glass sheet associated with it. Preferably however, they are mixed or milled into the plastic before sheeting.

In the accompanying drawings:

Figure 1 is a sectional perspective view of one form of phototropic, plastic body or interlayer of the invention;

Figures 2 to 7 are similar views of various forms of multilayer phototropic units embodying the invention; and

Figures 8 to 10 are transmission curves for specific forms of phototropic units.

In considering the present invention in detail it is important to understand that it was heretofore believed that while a number of different transparent resins could be used as carriers for the metal dithizonates, the carrier employed must be free from nitro groups, hydroxyl groups, amine groups and methacrylate monomers. This was because it was thought that such groups or monomers would act to inhibit color change.

However, the most important and the most potentially valuable of presently used and contemplated plastic interlayer materials for laminated safety glass all include one or another or more of these groups or monomers;

and, in accordance with this invention, these interlayer materials can, when properly and sufficiently plasticized with a compatible plasticizer, and properly combined with metal dithizonates be rendered highly and efficiently phototropic.

By way of a preferred example only, and in no way to be interpreted as a limitation, polyvinyl butyral (PVB) which is used almost exclusively in the present day manufacture of laminated glass, when plasticized to an extent common in the laminated glass art with PEP (di (iso-decyl) 4, 5-epoxy tetrahydrophthalate), is rendered phototropic by incorporating into the plasticized resin, prior to forming it into a sheet, from .01% to 2.0% by weight of diphenylthiocarbazonemercury-para-anisole (DZ-Hg-p-anisole).

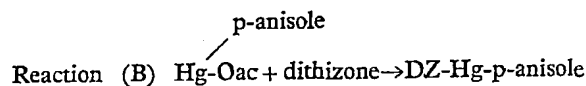
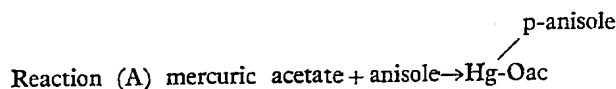
In thicknesses common in automotive laminated safety glass (.015") such a plastic layer is yellow in color and, when exposed to sunlight, darkens rapidly, assuming a uniform dark blue color in about 25 seconds. When shielded from the sun and at room temperature it rapidly reverts to the original lighter and more transmissive yellow color, a noticeable change back occurring in less than 15 seconds and 100% reversion in approximately 5 minutes.

A representative and preferred procedure for producing a phototropic plastic sheet by this invention is described below and, because the manner of synthesizing the dithizonate has a definite effect on the properties of the finished product this will be considered the initial step in the procedure.

EXAMPLE

The dithizonate (Method 1)

The synthesis of diphenylthiocarbazonemercury-para-anisole (abbreviated DZ-Hg-p-anisole), for example, involves the following two major chemical steps:



The term "ac" in the above and following reactions represents the acetate radical.

The product of reaction (B) is the phototropic compound.

Reaction (A) Procedure

For the synthesis of the Hg-Oac intermediate, 43.2 g of Eastman EK No. 465 anisole and 32.0 g of mercuric acetate, re-

agent grade, were dissolved in 300 ml of glacial acetic acid in a one liter flask. The reaction was carried out with an air condenser and the flask heated in a bath maintained at 70° C. for 3½ hours. The hot mixture was poured into 1200 ml of distilled water with vigorous stirring for 1 hour using a magnetic stirrer in a 2000 ml flask. The white precipitate was vacuum filtered and washed with two 100 ml portions of distilled water and pressed dry. The solids were air-dried over-

night and then dispersed in 800 ml of hexane and refluxed on a steam plate for 15 minutes. The mixture was stirred at room temperature for 1 hour, cooled in an ice bath, vacuum filtered and the solids washed with two 100 ml portions of ice cold hexane. The precipitate was air-dried and then placed in a Soxhlet extraction for 12 hours. A 33 × 80 mm thimble, 2000 ml flask and 1000 ml of hexane were used in the operation. The remaining solids were air-dried and then recrystallized from 300 ml of methanol. The 8.7 grams of the para isomer obtained (24% yield) had a melting point of 181—2° C.

15 Reaction (B) Procedure

For the synthesis of the DZ-Hg-p-anisole p-anisole

compound, 5 grams of the Hg-Oac intermediate were dissolved in 250 ml of chloroform. Six drops of acetic acid were added, and then 3.2 grams of dithizone were slowly added over a ½ hour period, the solution being stirred magnetically. The resulting solution, which was a bright yellow-orange in color, was evaporated on a hot plate till cooling caused slight crystallization. Hexane was added to precipitate the product, about 1200 ml being required. The solution was cooled in ice and the bright orange product filtered off by suction. The product was redissolved in 30 100 ml of CHCl₃, heated till all was in solution, and again precipitated with 1200 ml of hexane, cooled in ice, filtered and dried at 80° C. over P₂O₅ under vacuum for 2 hours. The yield was 7.0 grams or 90% of the theoretical.

35 (Method II)

As an alternate procedure, Reaction A may be carried out by first refluxing a solution containing 15.0 grams of mercuric acetate, 20 ml of methanol and 90 ml of anisole for 3 hours. Then adding 20 ml of methanol and 2.5 grams of glacial acetic acid and refluxing the solution for 64 hours. Next the solvents are evaporated under a vacuum to leave a white crystalline solid which is ground up to a powder and slurried in distilled water repeatedly to remove any water soluble impurities. When the white powder is then filtered off and dried it will be found to have a melting point of 165—175°C. and will react readily with dithizone to yield a strong phototropic compound.

50 (Method III)

The dithizonate may also be formed (Reaction B) by an alternate procedure. This consists in shaking an aqueous solution of a reacting heavy metal with an immiscible organic solution of dithizone. Chloroform and carbon tetrachloride are suitable solvents, the dithizone being generally soluble in organic solvents which impart a violet, orange, red or yellow color.

The Plastic Sheet

A phototropic plastic sheet was produced by weighing out 0.0750 grams of DZ-Hg-p-anisole produced by Method I and dissolving it in 20 grams of di (iso-decyl) 4,5-epoxy tetrahydrophthalate (PEP) plasticizer. After the dithizonate was in solution the plasticizer was mixed thoroughly with 50 grams of polyvinyl butyral resin powder sold under the Regd. Trade Mark "BUTVAR" and this mixture was milled into a 12" × 18" sheet, .015" thick, on the mill at 275° F. for about 8 minutes.

The following additional metal dithizonates, falling under the probable structural formula set forth above wherein DZ is diphenylthiocarbazone, as well as many others, were produced by one or more of the three methods outlined:

DZ-Hg-Salicylate	
DZ-Hg-Citrate	
DZ-Hg-Succinimide	
DZ-Hg-(I)	
DZ-Hg-2,5 dichloro, 3,6-dihydroxy-p-benzoquinone	85
DZ-Hg-MoO ₄	
DZ-Hg-WO ₄	
DZ-Hg-naphthalene sulfonate	90
DZ-Hg-anisole	
DZ-Hg-gallate	
DZ-Hg-Cinnamate	
DZ-Hg-anthranilate	
DZ-Hg-salicylamide	95
DZ-Hg-mandelate	
DZ-Hg-4-aminosalicylate	
DZ-Hg-vanillate	
DZ-Hg-pyridine	
DZ-Hg-Mo-oxalate	100
DZ-Hg-W-gallate	
DZ-Hg-phosphomolybdic acid	
DZ-Hg-O-anisole	
DZ-Hg-dimethoxybenzene	
DZ-Hg-phenyl ether	105
DZ-Hg-thiophene	
DZ-Hg-aniline	
secondary DZ-Hg-(II) Cl	
DZ-Hg-CN	
DZ-Hg-phosphovanadomolybdic acid primary (in which one of the acidic hydrogens of dithizone is replaced) and secondary (in which both acidic hydrogens of dithizone are replaced).	110
DZ-Hg-SCN	115
DZ-Hg-Ferrocene	
DZ-Hg-P-methylanisole	
DZ-Hg-P-anisole	
DZ-Hg-P-anisole + H ₂ WO ₄	
DZ-Hg-P-anisole + H ₂ MoO ₄	120
DZ-Hg-p-chloroanisole	
DZ-Hg-p-fluoroanisole	
DZ-Hg-methylanthranilate	
DZ-Hg-pyrrolidone	
DZ-Hg-n-butylcrotonate	125
DZ-Hg-itaconate	

- DZ-Hg-methacrylate
- DZ-Hg-butyl acrylate
- DZ-Hg-O-fluorophenetole
- DZ-Hg-anisonitrile
- 5 DZ-Hg-benzil
- DZ-Hg-p-anisidine
- DZ-Hg-methacrylate chromic chloride
- DZ-Hg-p-nitroanisole
- DZ-Hg-anisyl alcohol
- 10 DZ-Hg-anisaldehyde
- DZ-Hg-methacrylic acid
- DZ-Hg-2,5 dimethoxyaniline
- DZ-Hg-vinylcyclohexane dioxide
- DZ-Hg-indole
- 15 DZ-Hg-ethylene diamene tetraacetic acid
- DZ-Hg-ethylene diamene tetraacetic acid-Fe
- DZ-Hg-1,4 dimethoxy-2-nitrobenzene
- DZ-Hg-anethole
- 20 DZ-Hg-2 ethoxynaphthalene
- DZ-Hg-carbazole
- DZ-Hg-3,3 dimethoxybenzidine
- Hg (HDZ)₂ (two dithizone groups attached to mercury atom)
- 25 DZ-Hg-2,5 dimethoxytolene
- DZ-Hg-p-methoxy-phenyl isocyanate

Also all of these, as well as the diphenylthiocarbazone mercuric anisole, were incorporated into interlayers of laminated safety glass units as described and all of the resulting units exhibited strong color change when tested for phototropic properties.

As has been indicated above, this invention is especially concerned with phototropic plastic bodies of the type in which the plastic carrier for the metal dithizonate contains nitro groups, hydroxyl groups, reactive amine groups or methacrylate monomers because the plastic materials that are most widely used or are potentially most important for use in laminated safety glass interlayers all contain one or more of these groups or monomers. Thus, polyvinyl butyral, which was employed in the examples above and is presently used almost exclusively as the interlayer material in commercially available laminated safety glass, contains many OH groups; and other promising interlayer materials presently under consideration for possible future use also contain at least one such group or monomer.

One of the features of this invention has to do with the way in which the phototropic resin is plasticized and this involves both the degree of plasticization and the type of plasticizer used. Thus, the chemical reactions within the plastic body both during the darkening and the fading color change require sufficient mobility in the medium for the mechanism to take place. In other words, the efficiency of the photochromic action in a plastic body is, to a notable extent, a function of its softness or degree of plasticization.

Generally speaking, from 25 to 45 parts by weight of plasticizer gives good phototropic

results in accordance with this invention and, when the plastic body is used as an interlayer for laminated safety glass it is preferred that plasticization be well within these limits to also obtain the best physical results. On the other hand, if the plastic body is to be used alone and/or in greater thicknesses, something less than 25 parts plasticizer may be used; or, for special uses more than 45 parts can be used. However, it must be appreciated that as the amount of plasticizer is increased beyond the upper limit the plastic sheet becomes progressively and, ordinarily, objectionably softer; and as the plasticizer is decreased below the lower limit the phototropic action will be slowed down appreciably, especially in the fading or reversion cycle of the color change.

Similarly, the type of plasticizer employed is important and, while in making laminated safety glass units all of the commonly used plasticizers will produce workable phototropic units, more efficient and stable units can be had by a proper selection of plasticizers. For example, in the commercial manufacture of laminated safety glass polyvinyl butyral interlayers are generally and preferably plasticized with 3GH (di-2-ethyl butyrate triethylene glycol), and may be so plasticized in making a phototropic unit of this character. However, the life of such a laminated phototropic unit can be extended by simply employing a different plasticizer. For example a laminated unit, made up of two $\frac{1}{8}$ " sheets of iron containing, heat absorbing glass with an interlayer of .015" polyvinyl butyral plasticized with 3GH and rendered phototropic by milling a metal dithizonate into the interlayer, was tested along with a unit that was identical, except that the resin was plasticized with di (isodecyl) 4,5-epoxy tetrahydrophthalate (PEP), by exposing them 45° to the south in direct sunlight. The unit with the PEP plasticized interlayer had an effective life more than 10 times as long as the 3GH plasticized one.

Other plasticizers that have been employed in the same way and which when tested have been found to give the units effective lives varying in lengths from that of 3GH to that of PEP are:

- di-2-ethylbutyrate triethylene glycol
- dibutyl sebacate
- dibutylethylene glycol ethyl ether adipate
- epoxy tallate
- tributyl citrate
- tris-betachloroethyl phosphate
- di-2-ethylhexyl adipate
- 120 "Benzoflex 2-45" which is diethylene glycol dibenzoate
- those derived from soya bean oils
- dibutyl isosebacate
- 125 dioctyl phthalate
- diethylene glycol diperargonate
- di-isobutyl adipate

TABLE

Laminate No.	Configuration	Initial Transmittance		
		Light	Dark	Range
1	RP-(I)-RP-Filter A-EZ	55.3	14.8	40.5
2	RP-(II)-RP-Filter A-EZ	55.8	15.9	39.9
3	RP-(I)-Filter B-EZ	57.8	16.4	41.4
4	RP-(II)-Filter B-EZ	57.9	16.1	41.8
5	RP-(I)-Filter B-RP	65.0	18.5	46.5
6	RP-(II)-Filter B-RP	65.7	22.2	43.5
7	EZ-(I)-EZ	51.8	13.8	38.0
8	EZ-(II)-EZ	52.0	17.2	34.8
9	RP-(II)-RP-Filter A-RP-Film	32.9	11.0	21.9
10	RP-(II)-RP-Film	31.0	10.9	20.1

In the "Configuration" column in the above table, "RP" denotes a sheet of regular plate glass and "EZ" a sheet of high iron glass; the Roman numerals denote a phototropic plastic interlayer made by the method numbered correspondingly in the Example above; "Filter A" and "Filter B" denote particular ultra violet light filters; and "Film" denotes a transparent, reflecting film. Laminates designated as 1 and 2 (illustrated in Fig. 4 of the drawings) and laminate designated 9 (illustrated in Fig. 6) were made up with three glass plies 14. All of the others (illustrated in Figs. 3, 5 and 7) were made with two glass plies 12 and 13.

In laminates 1 and 2 (illustrated in Fig. 4), 3 to 6 (illustrated in Fig. 5) and 9 (illustrated in Fig. 6), UV filters 15 of two different compositions, depending upon their position in the laminates, were used. "Uvinul D-50", purchased from General Aniline and Film Corporation, New York, New York, U.S.A. was used as the filter material in both and "Filter A" was made by milling 50 grams of Butvar (Regd. Trade Mark), 20 grams 3GH, 0.2100 grams of "Uvinul D-50" and 0.0500 grams of paraoctyl phenol into a .015" sheet. "Filter B" was identical except that 20 grams of PEP was used as the plasticizer. Filter B was used where the filter sheet was

placed in contact with the phototropic interlayer (laminates 3 to 6, illustrated in Fig. 5) because, as explained above, the phototropic material in contact with PEP has a longer effective life.

The heat rejecting films 16 of laminates 9 and 10 (illustrated in Figs. 6 and 7, respectively) were blue films of Sn-Sb composition sprayed on the glass and had a transmittance of 45%.

The figures in Table A present the exposure data in percent of light transmittance as the laminates were examined at various intervals up to 1000 hours in a single arc weatherometer. The readings during the exposure period were all taken in the light or unexcited state but initial and final transmittances are in both the light and dark condition. Dark readings were taken as quickly as possible but, since fading starts immediately, these readings are not the exact minimum. The range is the difference between the light and dark readings. Similar data are presented on the laminates after the 1000 hours exposure. The last two columns show the loss in transmittance by fading during the exposure in the light and dark condition. After 578 hours, the exposure was discontinued for a period of two months and then resumed.

The results of the exposure, as observed by

Transmittance After Hours Exposure in Weatherometer — Light								Final Transmittance			Loss in Trans- mittance After 1000 Hrs.	
104	245	386	466	578	707	843	1000	Light	Dark	Range	Light	Dark
57.8	58.5	59.8	61.1	62.1	59.1	61.2	62.2	62.2	33.3	28.9	6.9	18.5
58.7	60.0	60.9	62.1	62.9	60.8	62.7	63.1	63.1	32.8	30.3	7.2	16.9
60.0	59.0	62.7	63.1	64.0	60.9	63.9	64.8	64.8	35.8	29.0	7.0	19.4
61.2	61.5	64.9	65.0	65.9	63.9	65.2	66.8	66.8	42.1	24.7	8.9	26.0
67.2	66.2	68.7	70.1	71.1	68.2	71.2	71.9	71.9	39.1	32.8	6.9	20.6
68.9	67.8	70.2	70.8	71.9	68.1	70.9	72.0	72.0	38.7	33.3	6.3	16.5
53.9	52.8	55.2	56.1	57.8	57.8	58.2	58.9	58.9	41.0	17.9	7.1	27.2
56.2	55.0	57.8	58.2	59.1	59.2	60.8	61.9	61.9	49.0	12.9	9.9	31.8
33.2	34.4	34.9	35.1	35.2	33.2	35.1	35.0	35.0	16.9	18.1	2.1	5.9
33.9	33.0	34.0	34.6	34.9	34.9	35.0	35.2	35.2	23.2	12.0	4.2	12.3

comparing the loss in transmittance for the various configurations, show, inter alia, that:

- 5 (a) The combination of film and filter is very effective in retarding fading, with the loss over 1000 hours being 2.1% and 5.9% in the light and dark forms, respectively.
- 10 (b) The reflecting film gives more protection than does the filter, each by themselves (compare laminates 6 and 10).
- 15 (c) The use of three glass plies with separated filters appears to have no great advantage over two plies with the filter in contact with the phototropic sheet (compare laminates 1 and 2 with 3 to 6). However, the effect of the filter is very positive as shown by comparing laminates 9 and 10.
- 20 (d) Each laminate containing a filter in any location recovered significantly during the two month rest at 578 hours. None of the others did.

25 It was also observed that the orange color in the unexcited yellow plastic is unstable and fades out quickly in the sun or weatherometer leaving a lighter yellow but with no significant effect on the density of the excited blue color; the use of a blue film 16 definitely toned down the yellow color; and after the 1000 hours exposure, all ten laminates still colored in

bright sunlight and faded in the dark at the normal rate.

Following the exposure tests recorded in Table A, additional tests designed to show the effectiveness of coloring dyes as decomposition retarders were made. The results of these are shown by transmission curves in Figs. 8 to 10 of the drawings and are based on the knowledge that light rays in the area of the spectrum between about .3 and .45 microns are the ones that cause the most rapid decomposition of and resulting loss of effectiveness in the phototropic metal di-thizonates.

Thus, as seen in Fig. 8, a sample made as shown in Fig. 3 and with the interlayer 10' made up of 50 grams of polyvinyl butyral plasticized with 20 grams of PEP and rendered phototropic by having .0750 grams of DZ-Hg-p-anisole milled thereinto and with no decomposition retarder except the glass in the lamination shows a definite reduction of transmittance in the critical area with a peak transmittance of approximately 30% in the .37 to .40 micron area.

However, when an interlayer prepared in the same way, but with .2800 grams (0.4%) of the ultra violet filter material added, is used, the transmission in the critical area of the spectrum is sharply reduced as shown by

the full line 17 in Fig. 9. Additional improvement, with relatively slightly reduction in the visible, is obtained by adding .7000 grams (1.0%) of the filter material as illustrated by the broken line 18 in the same figure; but practically no further improvement results when the amount of filter material is increased beyond that point. In fact, 1.4000 grams (2.0%) gives a curve substantially the same at that shown at 18.

On the other hand, when much smaller amounts of a yellow dye are added, instead of the filter material, to the interlayer a surprising reduction in transmission in the critical area is noted. Thus, Fig. 10 illustrates the result of adding only .0500 grams (.07%) of a yellow dye (sold by National Aniline Co., New York, New York, U.S.A., as Plasto Yellow MGS) to the interlayer. The addition of an increased amount of the dye (.1000 grams or .14%) gives an even flatter curve between .3 and .5 microns and, when .3000 grams (.43%) is used, the curve appears to be completely flat between these points and with practically no loss in visible transmission.

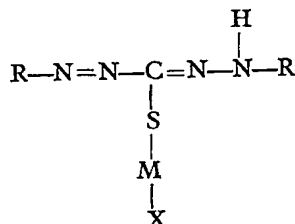
In view of the remarkable performance of the dye and the relative facility with which it can be incorporated into any type of unit from a single layer of phototropic plastic to the most involved glass-plastic type lamination, it is generally preferred as the decomposition retarder.

In selecting the dye it is only necessary that it be compatible with the materials with which it is to come in contact and that it be of a color generally in the yellow-orange region, with the most efficient being those of a yellow, or yellow toward orange color.

Where, as is the case with the mercuric dithizonates, the phototropic body is of a yellowish color, the addition of a yellow to orange dye does not materially alter the appearance of the unit and, in any event, some modification of the color to improve or enhance appearance or to tone the unit into its environment can be had, as indicated above, by the use of transparent, reflective films 16 of materials that will provide the desired complementary or modifying color.

WHAT WE CLAIM IS:—

1. A phototropic unit comprising a body of plastics material combined with a metal dithizonate rendering said body phototropic and having the following structural formula:



where M is an element selected from the group consisting of bismuth, cadmium, cobalt, copper, gold, indium, iron, lead, manganese, mercury, nickel, palladium, platinum, polonium, silver, tellurium, thallium, tin and zinc; where R is an aryl group; and X is a radical containing a group selected from those consisting of carboxyl, ether, ester, amide imide, nitrile, anhydride, amine, nitrate, acrylate, methacrylate, pyridyl, sulfonate, isocyanate, thiocyanate, cyanide, molybdate and tungstate.

2. A unit as defined in Claim 1 in which said plastics material is a sheet of synthetic resin containing at least one of the following:

an hydroxyl group
a amine group
a nitro group
a methacrylate monomer

and is plasticized with from 25 to 45 parts by weight to 100 parts of the resin of a compatible plasticizer.

3. A unit as defined in Claim 2 in which said plastics material is a sheet of polyvinyl butyral.

4. A unit as defined in Claim 3 in which said polyvinyl butyral is plasticized with di (iso-decyl) 4,5-epoxy tetrahydrophthalate.

5. A unit as claimed in any one of Claims 1 to 4 wherein the dithizonate is a mercuric dithizonate wherein DZ is diphenylthiocarbazone and which is selected from the group consisting of:

DZ-Hg-citrate
DZ-Hg-succinimide
DZ-Hg-MoO₄
DZ-Hg-WO₄
DZ-Hg-cinnamate
DZ-Hg-pyridine
DZ-Hg-Mo-oxalate
DZ-Hg-phosphomolybdic acid
DZ-Hg-thiophene
DZ-Hg-CN
DZ-Hg-SCN
DZ-Hg-Ferrocene
DZ-Hg-p-anisole
DZ-Hg-p-anisole + H₂WO₄
DZ-Hg-p-anisole + H₂MoO₄
DZ-Hg-pyrrolidone
DZ-Hg-n-butylcrotonate
DZ-Hg-itaconate
DZ-Hg-methacrylate
DZ-Hg-butylacrylate
DZ-Hg-methacrylate chromic chloride
DZ-Hg-methacrylic acid
DZ-Hg-vinylcyclohexane dioxide
DZ-Hg-3,3 dimethoxybenzidine

rendering said body phototropic.

6. A unit as defined in Claim 1 in which said dithizonate is diphenylthiocarbazone-mercury-para-anisole.

7. A unit as defined in Claim 1 in which said body of plastics material is a sheet of polyvinyl butyral plasticized with di (iso-decyl) 4,5-epoxy tetrahydrophthalate, and said dithizonate is a mercuric dithizonate. 35
8. A unit as defined in Claim 1 in which said body of plastics material is a sheet of polyvinyl butyral plasticized with di(iso-decyl) 4,5-epoxy tetrahydrophthalate, and said dithizonate is diphenylthiocarbazone-mercury-para-anisole. 40
9. A unit as defined in Claim 1 and including a decomposition retarder for said dithizonate which comprises at least one member of the group consisting of a sheet of glass, an ultra violet filter, a transparent heat reflecting film, and a yellow dye. 45
10. A unit as defined in Claim 9 in which said body of plastics material is a sheet of polyvinyl butyral plasticized with di(iso-decyl) 4,5-epoxy tetrahydrophthalate, said dithizonate is diphenylthiocarbazone-mercury-para-anisole and said retarder is a yellow dye. 50
11. A unit as defined in Claim 9 in which said body of plastics material is in sheet form and said retarder is at least one sheet of glass heat and pressure laminated to said plastic. 55
12. A unit as defined in Claim 11 in which said glass is high iron glass.
13. A unit as defined in Claim 9 in which said body of plastics material is in sheet form and said retarder includes spaced sheets of glass, and an ultra violet filter heat and pressure laminated with said plastic between said glass. 35
14. A unit as defined in Claim 11, and having a transparent heat reflecting film associated with said lamination.
15. A unit as defined in Claim 9 in which said body of plastics material is a sheet plasticized with a compatible plasticizer, said retarder comprises a yellow dye, and said dithizonate and said dye are mixed with the plastic in said plasticized sheet. 40
16. A unit as defined in Claim 9 in which said body of plastics material is a sheet of polyvinyl butyral plasticized with di(iso-decyl) 4,5-epoxy tetrahydrophthalate, said dithizonate is diphenylthiocarbazone-mercury-para-anisole, and said retarder comprises sheets of glass heat and pressure laminated to opposite surfaces of said plasticized sheet of plastics material. 45
17. A unit as defined in Claim 16 in which at least one of said sheets of glass is a sheet of high iron glass. 55
18. A phototropic unit according to Claim 1 and as set forth in the specification with reference to the accompanying drawings.

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COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of
the Original on a reduced scale
Sheet 1

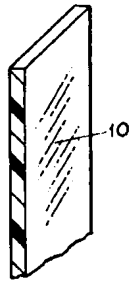


Fig. 1.

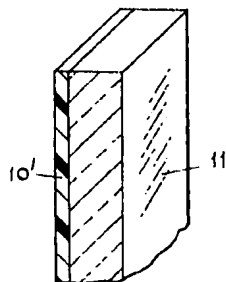


Fig. 2.

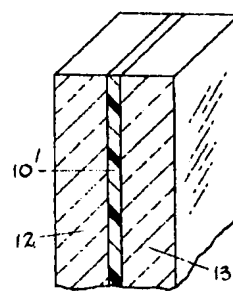


Fig. 3.

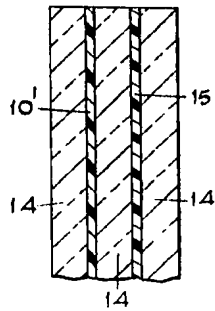


Fig. 4.

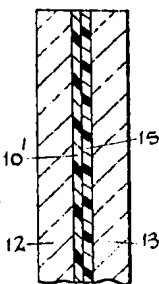


Fig. 5.

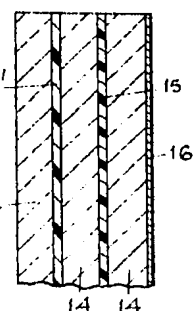


Fig. 6.

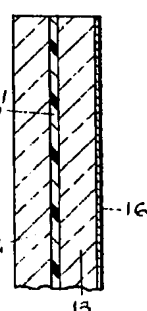


Fig. 7.

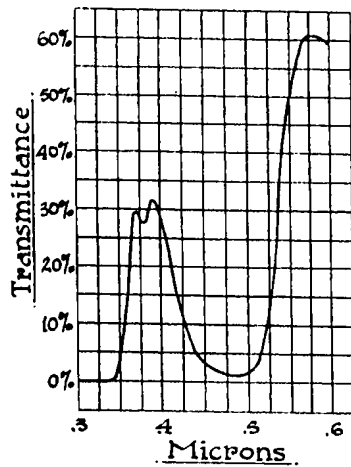


Fig. 8.

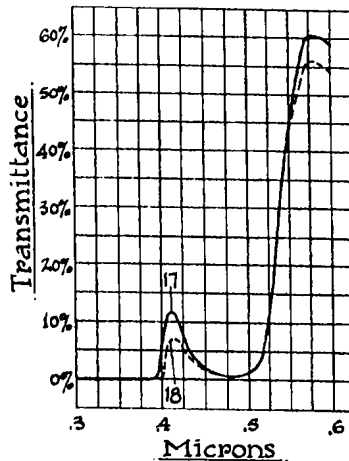


Fig. 9.

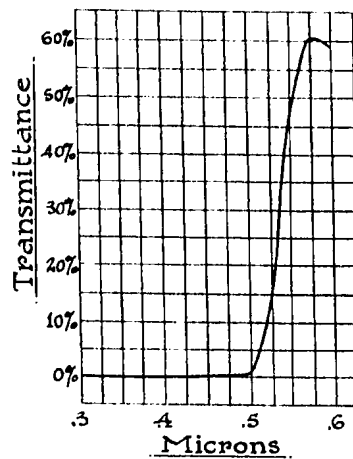


Fig. 10.